

### DESCRIPTION

### METHOD FOR TREATING OF OILS AND FATS

#### FIELD OF THE INVENTION

The present invention relates to a method for treatment of oils and fats, in particular, relates to a method for treatment of oils and fats characterized by making it possible to reuse a-treated wasted oils and fats or a-treated discharged oils and fats not depending on containing ratiothe amount of saturated fatty acid unsaturated fatty acid.

### DESCRIPTION OF THE PRIOR ART

Presently, there are many sorts of wasted oils and fats in Japan. For example, tallow, bovine born oil, bovine internal organ oil-of bovine, lard, pig bone oil, pig internal organ oil-of pig, chicken oils and fats, residue oil formed at a refining process of animal oils and fats or vegetable oils and fats, animal foots oil or vegetable foots oil formed atfrom rendering of animal oils and fats or vegetable oils and fats, strong alkaline dark oil formed at a treating process of a foots oil, various wasted animal oils and fats or vegetable oils and fats discharged from a foodsfood processing factory, waste oils and fats discharged from production process of purified oil for <del>foods</del>food as a by-product, for example, discharged oil generally called as "oil foots" at a producing process of beans oil, rapeseed oil or corn oil or waste foods oil such as waste oil from deep-fried food processing. Now a days Nowadays, it is said that the total amount of these waste oil ofoils for a year is more than 10 million tons or more than 20 million tons.

Further, from a disturbance the occurrence of mad cow disease, it became necessary to treat and burn up bovine originatedbovine-originated oils and fats separately from other oils and fats. However, since calories of bovine originated bovine originated oils and fats is high, the durability of a burning furnace becomes problem, a problem and safe burning up of it can not cannot be expected. Therefore, it is obligated was necessary to preserve waste bovine originated oils and fats separately until a treating method iswas developed, however, actually, bovine originated bovine-originated oils and fats is are mixed with other oils and fats and isare not controlled as obligated. Therefore, a development of a new treating method is becoming a pressing subject.

Regarding animal oils and fats, except bovine originated for bovine-originated oils and fats, although a part of it is used as a fodder offor a domestic animal, foods or cosmetic composition, mainly mostly is burned up. And, regarding. Regarding residue oil formed at a refining process of animal oils and fats or vegetable oils and fats for foodsfood, since said residue oil is mainly a-strong alkaline waste oils and fats, the durability of an ordinary furnace is a problem and, accordingly, a—treatment by burning up—is impossible.

A part of waste <del>foods</del>food oil is used as a fuel <del>of</del>for Diesel engines by converting by the "methylesterfication method". This method can be illustrated as follows. That is, methanol or ethanol and sodium hydroxide are mixed towith a waste foods food oil with constant stirring, then the mixture is left for standing to stand. Glycerin or others, which are impurities, are absorbed by methanol or ethanol and separated separate to an upper side when staying maintained in a standing state. And oilOil, which is located at a lower side, is used as a fuel. However, this method can only be applied for the refining of high quality waste foods oil, food oil and cannot be applied for refining of middle quality waste **foods**food oil, low quality **foods**food oil or mud waste foots oil. The reason why can be illustrated as follows. That is, the "methylesterfication method" is a technique developed 50 or 60 years ago to convert a virgin oil such as soy bean oil or rapeseed oil to a fuel and can not cannot be applied to

ana used waste foods food oil which is characterized in that the oxidation degree is has progressed to a higher level. Therefore, middle quality waste foodsfood oil, low quality foods food oil or mud waste foots oil are omitted from the object of refining by this method. Further, oils and fats ofhaving a high containing ratio of saturated fatty acid isacids are out of the discussion. Furthermore, a method of "conversion of waste foods food oil, fish oil to Diesel engine fuel by ozone treatment, is also applied. This method is a technique objected to for oils and fats whose containing ratio of saturated fatty acidacids is high (for example, soy beans oil, rape seed oil, corn oil, camellia oil or fish oil).

SaidThis method is a technique to pourof pouring materials to be treated (oils and fats characterized in that contents the content of unsaturated fatty acid is high) into a reaction tank and ozone is added from a lower position of the reaction tank, then athen, the double bond of the unsaturated fatty acidacids is dissociated by oxidization forth of ozone, by ozone and thus converts the material to a fuel. Therefore, a waste oil whose contents content of unsaturated fatty acid is high (high quality, middle quality, low quality and mud oil) can be refined by this method, however, oils and fats whose melting point is high and concentration of saturated fatty acidacids is high, such as palm oil, residue oil of palm oil, coconut oil or residue oil of coconut oil can notoil, cannot be treated by this method. Further, said method can-not cannot be applied to a strong alkaline waste oil too. For example, in a case when oils and fats whose contents content of saturated fatty acidacids is high is treated by this method, large amount of ozone is added to dissociate the double bonds of the fatty acid. And when addingWhen the amount of ozone becomeadded becomes large and the time to add of adding also becomes long, consequently, the saturated fatty acid causes acids cause polymerizing reaction reactions by the ozone reaction. Said The polymerizing

reaction means the reactions mean a state that the oils and fats causes caking.

Oils and fats can be roughly classified to ainto saturated fatty acidacids and unsaturated fatty acidacids.

When the content of saturated fatty acidacids becomes large, the melting point and caking ratio become high and solidifiedsolidification occurs quickly. As oils and fats whose content of saturated fatty acidacids is larger than 80%, tallow (Fedd oil), bovine born oil, pig oil (lard), pig bone oil, chicken oil, sheep oil, goat oil or horse oil can be mentioned. And asAs a vegetable oil, palm oil, residue oil of palm oil, coconut oil and residue oil of coconut oil can be mentioned.

As oils and fats which <u>contains</u> contain more than 80% of unsaturated fatty <u>acidacids</u>, soy <u>beans</u>bean oil, rape seed oil, sunflower oil or corn oil can be mentioned as a vegetable oil, and fish oil can be mentioned as an animal oil.

Because unsaturated fatty <u>acidacids</u> can be more easily treated than <u>saturated</u> fatty <u>acidacids</u>, the development has been progressed on oils and fats whose content of unsaturated fatty <u>acidacids</u> is high.

## SUMMARY OF THE INVENTION

The present invention relates to a treating method of oils and fats and the object of the present invention is to provide a material for various oils and fats, such as a fuel, by treating oils and fats whose contents of saturated fatty acidacids is high.

The gist of the present invention is a treating method of oils and fats characterizing to carrycharacterized in carrying out ozone treatment and light irradiation treatment treatments on oils and fats of in a state of just prior to hydrolysis.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig.\_1 is a flow sheet illustrating processes process of the present invention, Figs. 2 and 3 are

illustratingillustrate views of a treatment apparatus of the present invention. Fig. 4 is an illustration view of a light irradiation apparatus of the present invention, Fig. 5 is an illustration view of another example of a treatment apparatus of the present invention. MarksThe numerals in the drawing are illustrated as follows.

- 1. Material tank, 2. First pre-treatment tank,
- 3. Second pre-treatment tank, 4. Pre-filtration filter press,
- 5. Pre-coating tank, 6. Oil separator, 7. Special ray irradiation device, 8. First treating tank, 9. Cooling chiller, 10. Second filtration device, 11. Pre-coating tank,
- 12. Second treating tank, 13. Third filtration device,
- 14. Pre-coating tank, 15. Regulating tank,
- 16. Cartridge tank, 17. Vapor generating device,
- 18. Ozone generating device, 19. Ozone inserting opening,
- 20. Material gas pipe, 21. First tank (liquidizing tank),
- 22. Second tank (liquid recovering tank), 23. Filtration device, 24. Liquefied gas fuel tank, 25. Stirrer
- 26. Filter, 27. Lubricating oil recovering device

# DESCRIPTION OF THE PREFERRED EMBORYMENTEMBODIMENT

The present invention will now be illustrated in more in detail.

Regarding waste oils and fats and discharged oils and fats which can be treated by the present invention, it is possible to be treated nottreat them without considering athe containing ratio of saturated fatty acids unsaturated fatty acidacids. Waste oils and fats of the present invention means oils and fats which is are treated by alkali or refined during a rendering process, however, also not treated oils and fats can also be treated. Specifically, animal oils such as tallow (Fedd oil), bovine bone oil, pig oil (lard), pig bone oil, chicken oil, sheep oil, goat oil, horse oil or fish oil or a vegetable oil such as palm oil, residue oil of palm oil, coconut oil and residue oil of coconut oil, soy beansbean oil, rape seed oil, sunflower oil or corn oil can be mentioned.

Further, regarding an ozone treatment, since the double bond or triple bondbonds of saturated fatty acid or unsaturated fatty acid becomes acids become easy to dissociate by light, ozone is inserted injected from a lower part of each treating reaction tank, tank and specific treatment is performed on an ozone inserting injection opening so as to progress that the ozone reaction progresses smoothly. Said The specific treatment means that a metallic net having 0.5 µm to 1 µm openings is equipped provided in a pipe of ezone inserting an ozone-injection opening. By equipping providing said fine metallic net, the ozone is divided to into ultra fine bubbles and the reaction can be progressed progress smoothly.

These waste oils and fats or discharged oils and fats (shortened to simply oils) should be set to a state of just prior to hydrolysis. For the purpose to set to a setting the state of just prior to hydrolysis, it is necessary to add moisture (vapor) to the oils and to carry out heat treatment and is desirable to press byuse a pressure of 3-10 atoms aimingatmospheres to shorten the treating time. By setting to a state of just prior to hydrolysis, stable saturated fatty acid becomes to acids become easier reactionable state to react by light irradiation and by ozone treatment.

Ozone treatment and light irradiation treatment are carried out on the oils set towhich are at a state of just prior to hydrolysis. Either ozone treatment or light irradiation treatment can be carried out first. Regarding the light irradiation treatment, it is desirable to change the wave-length of the light to be irradiated according to a sortthe type of the oilsoil, for example, in a case to produce of producing Diesel engine fuel from tallow, a desirable wave-length of light is 155nm to 325nm, which belongs to the domain of ultra violet, furtherultraviolet. Further, according to the power of a ray ray-generating source, light of 185nm to 256nm can be used. Furthermore, in a case to produce of producing an oil which does not solidify at approximately 0°C, which is used in foodsfood processing or

cosmetic composition processing, it is possible to cause a cleavage reaction and to-produce an oil which does not solidify at approximately 0°C by combining ultra violetultraviolet light, visible light and infra redinfra-red light of 356nm-405nm-800nm.

### **EXAMPLE**

## Example 1

As an Example of the present invention, athe flow sheet of Fig. 1, which relates to a process to produce of producing Diesel engine fuel from tallow, will be illustrated. Figs. 2 and 3 illustrate an equipment of the present invention and, however, isare not intendingintended to restrict the scope of claims of the present invention.

- (a) Material is supplied to a material tank (1) of approximately 20L capacity. Various sortsoils can be mentionedused as athe material, and the material is heated in the material tank according to the purpose of the treatment. Material The material is regulated by adding 3-5% of water to the total amount of the material if necessary.
- (b) The regulated oil is transferred to a first pre-treatment tank (2). The first pre-treatment tank (2) has a capacity of approximately 20L, which is the same volume toas the material tank. Since the purpose is to produce Diesel engine fuel from tallow, 3-8% of vapor to the total amount of the material is blown from the lower part of the tank so as to programcontrol the temperature to 120°C-130°C, and ozone, which is generated from an ozone generating device (18), is introduced from the lower part of the tank. This pre-treatment reacting apparatus is <del>pressed by</del>at a pressure of 1-2 atomsatmospheres and stirred well. The material is reacted to a state of just prior to hydrolysis. For the purpose to shortening the treating time, it is possible to presspressurize the apparatus to 3-10 atomsatmospheres. Further, this reacting apparatus is heated to 150°C-250°C and 5-8% or 10% of vapor to the total amount of the material is added and ozone is introduced. After

this process, said reacting apparatus is vacuumed toput under a vacuum of minus 2-3 or 5 atomsatmospheres and vapor (water) used in the previous process is removed. Thus, the material is reacted to a state of just prior to hydrolysis.

(c) Then the material, which is in a state of just prior to hydrolysis in the first pre-treatment tank, is poured into a second pre-treatment tank (3). To the material poured into the second pre-treatment tank (3), a stirrer which can pulverize the material to ultra fine particles and stir it byat a rotating speed of 300-400 r.p.m. The stirrer, which can pulverize the material to ultra fine particles, of the present invention is characterized in that a stainless steel wire blushbrush is equipped at a pointed end of the stirrer or using a propeller processed to have sawteetha sawtooth shape.

By providing a heater equipped-towith the equipment of the present invention, humidhumidity (vapor) which can not cannot be removed by a vacuum process is removed by heating. Said The heating is carried out at the temperature of 95°C-100°C or 100°C-120°C. Impurity is Impurities are extracted from the material oil, which is staying in a state of just prior to hydrolysis. For the purpose to remove of removing impurities, the material oil is passed passes through a first filtration device. And device and, during said process, ozone is added from the lower part of the equipment. During the process to adding ozone and to promote oxidization, for the purpose to oppress theof suppressing excess oxidization, 1-2% of sawdust or woody tips to the total amount of the material areis added.

(d) First filtration device: Material which has passed through the second pre-treatment process is passed passes through the first filtration device for the purpose to remove impurity of removing impurities extracted in the second pre-treatment process, such as glycerin or an absorbing agent added atto the process, such as woody tips-added at the process, are removed. The first filtration device is consisting consists of a prefiltration filter press (4), a filtering cloth of the prefiltration filter press (4) is coated with an absorbing agent such as activated clay, diatomaceous earth, zeolite or activated carbon. Accordingly, impurities formed atin the second pre-treatment device is are absorbed and removed. The amount of the absorbing agent is 1-3% to the total amount of the material or, according to a sort the type of material, 2-6% to the total amount of the material.

(e) Oil separator: The purpose of an oil separator is to remove humid more perfectly humidity remaining at from the previous vacuum dehydration process. That is, material contained in the second pre-treatment device is filtrated filtered by the first filtration device and flownsent to the oil separator (6). The oil separator is aiming to remove removes emulsified water remaining in the second pre-treatment device. Said The emulsified water is originated originates from humidhumidity (vapor) that is used in the material tank and in the first pre-treatment device and is not removed by the second pre-treatment device.

Shape The shape of the oil separator is cylindrical. Material is poured into the cylinder and discharged to the outside of the cylinder. This cylinder is specifically processed. Namely, the diameter of holes to pass through is becoming become larger from an inner side toward an outer side. Diameter The diameter of hole the holes of the innermost side is 1µm and the diameter of hole the holes of the outermost side is from 20µm to 30µm and, and by enlarging the size of the fine particles (clusters) of emulsified material (oil water), oil and water is instantly separated when discharged to the outside of the cylinder.

Separated oil is progressed progresses to the next process. And and separated water is transferred to a vapor generating device for the purpose toof reuse after filtrated being filtered by activated carbon.

(f) Special ray irradiation device: Material (oil), after water is separated, is <u>flownsent</u> into a special ray irradiation device (7). In a case to produceWhen producing

Diesel engine fuel from tallow, the wavelength of the light to be used in the present invention is a wavelength of ultra violet the ultraviolet domain of 155nm-325nm, further. Further, according to the power of athe ray generating source, light of 185nm to 256nm can be used. In a case to useWhen using oils and fats whose containing ratio of saturated fatty acid is high to thefor a use excepting except for fuel, for example, to produce an oil which does not solidifyingsolidify at approximately 0°C, which is used in <del>foods</del>food processing or cosmetic compounds processing, it is possible to cause a cleavage reaction and to produce said oil which does not solidify at approximately 0°C by combining ultra violetultraviolet light, visible light and infra redinfrared light of 356nm-405nm-800nm.

As a method for irradiation, a spiral wire of glass or silicone is wound around a ray source tube, and the material is flownflows along with the spiral wire from the upper side to the lower side so as to irradiate light. One example is shown in Fig. 4.

As the other method for irradiation, a method to  $\frac{irradiate}{of}$  irradiating by spraying the material in state of  $\underline{a}$ mist or fog, a dipping method, or a wet wall method can be used. Namely, it is important to expand the irradiation area.

FromFor the next step, the process is illustrated according to Fig. 3.

(g) First treating apparatus: In the case of fuelWhen producing fuel, the material after the process by a special ray irradiation device (7) indicates an igniting feature at this stage. And in the case of As for oils excepting not for fuel, the material after said process becomes does not to solidify at approximately 0°C. In the case of fuel producing, the purpose of the first treating tank (8) is to improve the quality as fuel, and in the case of oils excepting not for fuel, the purpose of the treatment is to enhance the value. To the transported material, 1-2% of rice-bran to the total amount of the material is added. Oil washing process by

rice-bran is carried out and, simultaneously, ozone is insertedinjected through an ozone inserting opening so as to carry out an ozone reaction. (18) is an ozone generating device.

- (h) Second filtration device: Inside of the second filtration device (10) is coated by onea cake layer selected from the group consisting of activated clay, diatomaceous earth, zeolite or activated carbon, which is transported from a pre-coating tank (11). By this cake layer, rice-bran added during the first treating process by 1-2% to the total amount of the material is removed and the quality of the oils is improved.
- (i) Second treating apparatus: Material after passedpassing through the second filtration device (10) is transferred to a second treating tank (12). Object The object of this tank is to improve the oils containing a high amount of a saturated fatty acid whose melting point is high, such as an animal oil, palm oil or vegetable oil not to solidify at thea temperature lower than 0°C. Material The material is cooled down by a cooling chiller equipped toprovided at the inside of the tank according to the purpose. Chilling The chilling temperature and the effect by chilling are as follows.

Material which has passed through each refining process is transported to a second treating tank and a second filtering device. When the material treated in the second treating tank is cooled down to 5°C by a cooling chiller, then passed through the second filtering device, the filtrated material does not solidify at thea temperature of from -7°C to -15°C in a refrigerator.

Material is cooled down to 10°C → does not solidify up to -5°C to -7°C.

Material is cooled down to 5°C → does not solidify up to -7°C to -15°C.

Material is cooled down from 0°C to 1°C → does not solidify up to -20°C to -30°C.

(j) Third filtration device: Inside of a third filtration device (13) is coated by onea cake layer selected from the group consisting of activated clay, diatomaceous earth, zeolite or activated carbon, which is transported from a precoating tank (14). Material after being treated by the second treating apparatus (12) is passedpasses through a cake layer of the third filtering device (13) and filtrated is filtered and introduced to ana regulating tank (15). Then the material is passedpasses through a cartridge tank and an aimed product is produced.

Physical The physical properties of the product obtained by conversion of tallow (Fedd oil) to Diesel engine fuel is summarized in Table 1 in comparison with a methylesterfication method and light oil on the market.

Table 1

	Tallow	Methylesterfication	Light oil
	after treated	method	
Calorific value	10.733	9500	10920
Cal/kg			
Density (15°C) g/cm <sup>3</sup>	0.888	0.888-0.90	0.835
Dynamic viscosity mm <sup>2</sup> /S	8	8-9	5-6
Flash point °C	37	130-140	66
Fluidizing point °C	-7.5	Max -5	- 8
Sulfur contents	0.0016	0.01	<0.2

Pig oil (lard oil) whose solidifying point (freezing point) is +30°C is refined by above-the above-mentioned apparatus and, and as a result, a liquid oil whose freezing point is -5°C is obtained.

## Example 2

In this Example, a method to obtaining lubricating oil or fuel to be used instead of gasoline will be illustrated based on Fig. 5.

Same The same as towith Example 1, according to the process shown in Fig. 2, (f) material after light irradiation treatment by a special ray irradiation device is transported to a first treating device (8). (in Fig.2, as far as In Fig. 2, a special ray irradiation device (7) is athe same apparatus.) 1) Material after the ray irradiation treatment is transferred to a first treating tank (8). After being transferred, 3-10% of a qas-qas-inducing agent to the total amount of the material is added to the material and stirred well. RotatingThe rotating speed of a stirthe stirrer is approximately 300 r.p.m. As a gas inducing gas-inducing agent, hexane-etc, etc., can be used. As the result of the light irradiation, hydro carbonhydrocarbon oil is formed by in a 20-30% ratio in the transferred material.

TeAt the inside of the first treating apparatus, a specially processed ozone inserting opening (19) is equipped, provided and from this opening, fine bubbles of ozone of 0.1µm-05µm size are blown in strongly and the blown in ozone emulsifyemulsifies the material instantly. From the emulsified material, <u>hydrocarbon</u> gas <del>of hydro carbons</del> is formed. The formed gas is transferred to a gas recovering apparatus mentioned below and liquefied. The liquefied product is almost the same as to-gasoline of a high octane value. Recovering The recovering ratio from the material is 40-50%,40-50% and 50-60% of the residue is lubricating oil.

Gas recovering apparatus

The gas recovering apparatus is composed of first tank (21), second tank (22) and a filtration device (23). First tank liquidates gas discharged from the first treating apparatus through a pipe (20) and second tank acts as a

recovering part of liquefied liquid. Functions can be illustrated as follows.

- (a) Gas discharged from the pipe (20) is introduced into  $\underline{a}$  spiral pipe formed  $\underline{in}$ —inside of the first tank (21).
- (b) A proper quantity of water is contained in the first tank (21), said water is kept at 0°C and by quenching, the gas is liquefied.
- (c) Aiming at smooth liquidation of the gas, a vacuum pump is equipped towith the second tank (22) (recovering part) and operate the vacuum pumpoperated to improve the recovering effect.

For the purpose to improve of improving the quality, the recovered liquid is filtrated filtered by a filtration device (23). As a method for filtration, filtration by a filter press, vacuum filtration or spontaneous filtration can be mentioned. As a filter, activated carbon, activated clay or zeolite can be used. The filtrated filtered liquefied gas fuel is preserved in a liquefied gas fuel tank (24).

Material remaining in the first treating apparatus causes a polymerization reaction by the effect of fine particles of ozone regulated to 2-5µm size discharged from an ozone inserting injecting opening (19) equipped toprovided at the lower part of the apparatus. Expecting To more rapidly and accurately cause the polymerization reaction, stirring is carried out. <del>Desirable</del>A desirable rotating speed is 10000-30000 r.p.m. However, if a stir tostirrer at the end of a rotating axis of which a special processed stirrer (25) is equipped provided, the rotating speed can be 300-360 r.p.m. As a The stirrer (25), is not restricted, however, when a stirrer characterizing by a wire <del>blush</del>brush of 0.1-0.3mm size is equipped at a pointed end of the rotating axis forming having a cross shape or a stirrer using a propeller processed to have sawteetha sawtooth shape is used, a remarkable effect can be obtained.

Filtration The filtration process is set—for the purpose to improve improving the quality of the polymerized

material. Filtrating The filtrating operation is carried out the same as to above the above-mentioned gas recovering process. That is, a filtering device (26) can be  $\underline{a}$  filter press, vacuum filtration or spontaneous filtration and, as a filter, activated carbon, activated clay or zeolite can be used. Polymerized The polymerized material, after the filtration process, is recovered at a lubricating oil recovering device (27).

From this treated material, a lubricating oil of a hardness of 10w-30~10w-40 for a gasoline engine or for a Diesel engine can be produced.

## APPLICABILITY FOR INDUSTRIAL USE

By the treating method of the present invention, oils and fats whose content of saturated fatty acid, which is recognized to be hard to refine, can be refined by a simple refining method and can be provided as a material for various oils and fats. That is, this method is suited to a treating method of oils and fats whose content of stable saturated fatty acidacids, waste oils and fats or, in particular, waste oils and fats originated linked to mad cow disease, and is useful to produce for producing Diesel engine fuel, lubricating oil or fuel and can be used instead of gasoline.